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Published
With international search report.

(54) Title: VERY HIGH MOLECULAR WEIGHT POLYETHYLENE

(57) Abstract

A very high molecular weight distribution can be prepared from a two component catalyst system. The polymer has a molecular weight range of from 1 x 10^6 to 25 x 10^6 and a molecular weight distribution range of 1.0 to 3.0

* See back of page

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VERY HIGH MOLECULAR WEIGHT POLYETHYLENE

Specification

This is a continuation-in-part of U.S. patent application Serial No. 133,480, filed December 22, 1987, which was a continuation-in-part of U.S. patent application Serial No 008,800, filed January 3, 1987.

Field of the Invention:

This invention relates to polymers produced by (co)polymerizing ethylene in the presence of certain catalyst systems described herein. More particularly, this invention relates to (co)polyethylene having a very high molecular weight and a narrow molecular weight distribution.

A method of preparing polymers, which includes the catalyst compositions and methods of preparing these catalysts, is set forth in full detail in copending U.S. patent application Serial No. 133,480 (also European patent application Serial No. 277,004, published August 3, 1988) and will not be repeated herein except to the extent necessary for clarity. However, the entire disclosure of U.S. patent application Serial No. 133,480 is expressly incorporated herein by reference. The disclosure does not exemplify polyethylenes having molecular weights in excess of about 1,000,000. Molecular weights in excess of 2,000,000 are not mentioned.

Background of the Invention

The production of polyethylene and its uses are well known in the prior art. It is also known that the physical properties of polyethylene (indeed any polymer) vary with its molecular weight. For example, very high molecular weight polyethylene--i.e., polyethylene with a weight-average molecular weight in excess of 1,000,000--has a low coefficient of friction and high abrasion resistance, impact toughness and tensile strength. Very high molecular weight polyethylene is used in rolling stock, materials handling, and fiber spinning from polymer gels.

Another characteristic which affects the physical

properties of a polymer is its molecular weight distribution, defined by the ratio of weight-average molecular weight (Mw) to number-average molecular weight (Mn). A polymeric product which has a broad molecular weight distribution, i.e., greater than about 5, will have certain undesirable characteristics. For instance, it is now realized when used in fiber spinning, polyethylene having both a broad molecular weight distribution and a very high molecular weight causes instabilities in the fiber spinning process.

The use of Ziegler-Natta type catalysts for the polymerization of ethylene to polyethylene is well known in the prior art. The traditional Ziegler-Natta type systems comprise a transition metal halide activated to a catalyst species by reaction with a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. The activation of these traditional Ziegler-Natta catalysts generates a variety of different active sites, each of which has its own rate of initiation, propagation, and termination. As a consequence of this non-uniformity of active sites, the catalysts linear polyethylene having a broad molecular weight distribution.

Recently, it has been found that active polymerization catalysts are formed when bis(cyclopentadienyl) compounds of the Group IV-B metals are used with methylalumoxane. As is well known, these systems offer several distinct advantages, in particular the production of polymers with narrower molecular weight distributions (Mw/Mn < 3) than those from conventional Ziegler-Natta type catalysts. These recently discovered catalyst systems, however, yield polymeric products having relatively moderate weight-average molecular weights, i.e., less than 500,000.

The need for a very high molecular weight polyethylene and preferably linear polyethylene having narrow molecular weight distribution is apparent.

Summary of the Invention:

In accordance with the present invention, very high molecular weight polyethylene, preferably high density, linear polyethylene having a narrow molecular weight distribution is produced. One method involves using a catalyst prepared by combining at least two components. The first component is a bis(cyclopentadienyl) derivative of a Group IV-B

metal compound containing at least one ligand which will combine with the second component or at least a portion thereof, such as a cation portion. The second component is an ion-exchange compound comprising a cation which will irreversibly react with the first component and an anion which is a single coordination complex capable of stabilizing the Group IV-B metal cation complex and sufficiently labile to permit displacement by ethylene during polymerization.

In the synthesis of the polymers of this invention, bis(cyclopentadienyl) hafnium-based catalysts are preferred and trialkyl- and/or -arylammonium salts of tetrakis(pentafluorophenyl)boron are the most preferred activators. These catalyst systems can produce polyethylenes having molecular weights in the range of about 5×10^5 and greater. In accordance with this invention it has been discovered that through pressure and temperature controls one can obtain polyethylene having molecular weight in excess of 1,000,000 and typically from 1×10^6 to about 25×10^6 with molecular weight distributions less than about 3. Typically the molecular weight distributions will be in the range of about 1.3 to about 3.0. These polymers are unique in that they combine a very high molecular weight with a very narrow molecular weight distribution. The preferred polymer has a molecular weight range from about 2×10^6 to 6×10^6 with a molecular weight distribution of about 2.0 or less.

Detailed Description of the Invention:

It has been discovered that very high molecular weight polyethylene having a narrow molecular weight distribution can be produced. The hafnium-based catalyst system used to produce the polymers of this invention are detailed in U.S. patent application Serial No. 133,480 which is expressly incorporated herein by reference.

The present invention relates to polyethylenes having both a very high molecular weight and a narrow molecular weight distribution. The term "very high molecular weight" is intended to encompass polymers having a molecular weight of about 1×10^6 and above. Preferably the polymers will have a molecular weight of

2×10^6 and above. In accordance with this invention, polymers having molecular weight up to about 25×10^6 and greater can be produced while maintaining the molecular weight distribution at about less than 3.

A surprising feature of this invention is that such very high molecular weight polyethylene polymers can be produced with a narrow molecular weight distribution. The molecular weight distribution is defined as the ratio of weight-average molecular weight to number-average molecular weight. For the purpose of this invention, a "narrow" molecular weight distribution means in the range of about 1.0 to about 3.0. Generally, the molecular weight distribution is about 1.3 to about 3 or less.

A catalyst useful for preparing such very high molecular weight polyethylene polymers is prepared by combining at least one first compound which is a bis(cyclopentadienyl) derivative of a metal of Group IV-B containing at least one ligand which will combine with a cation of the second compound which first compound is capable of forming a cation formally having a coordination number of 3 and a valence of +4 and at least one second compound which is a salt comprising a cation capable of donating a proton which will irreversibly combine with said at least one ligand (substituent) liberated by said Group IV-B metal compound and an ion which is a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and labile, compatible with and non-coordinating toward the Group IV-B metal cation formed from the first component, and capable of stabilizing the Group IV-B metal cation without interfering with said Group IV-B metal cations or its decomposition product's ability to polymerize ethylene.

The Group IV-B metal compounds, i.e., titanium, zirconium and hafnium compounds, useful as first compounds in the preparation of the catalyst capable of producing the polymer of this invention are bis(cyclopentadienyl) derivatives of titanium, zirconium and hafnium. The preferred Group IV-B metal compound is hafnium.

Compounds useful as a second component in the preparation of the catalyst used to make the very high molecular weight polyethylene of this invention will comprise a cation, which is a

Bronsted acid capable of donating a proton, and a compatible non-coordinating anion containing a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group IV-B cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by ethylene. The preferred second component is trialkyl- and/or -arylammonium salts of tetrakis(pentafluorophenyl)boron. Especially preferred second components are tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

The following examples are illustrative of the types of polymers that can be produced and are not intended to limit the scope of this invention:

EXAMPLE 1

In this example, ethylene was polymerized to linear polyethylene by adding to a 1 liter stainless-steel autoclave, previously purged with nitrogen and containing 400 ml of dry, deoxygenated hexane, first a solution containing 15 mg of bis(cyclopentadienyl)hafnium dimethyl in 30 ml of toluene, then, after 5 minutes, a solution of bis(cyclopentadienyl)hafnium dimethyl (12 mg) and tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron (30 mg) in toluene (50 ml). The autoclave was pressured with 90 psig of ethylene and stirred for 1 hour at 60°C. The autoclave was then vented and opened, and the polymer product isolated. The yield of polyethylene was 73.8 g. This material had a weight-average molecular weight of 1,123,000, a peak-maximum molecular weight of 1,097,000 and a molecular weight distribution of 1.78.

EXAMPLE 2

In this example, ethylene was polymerized by adding to an autoclave as described in Example 1 a solution of bis(cyclopentadienyl)hafnium dimethyl (9 mg) and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (3 mg) in toluene (10 ml). The autoclave was pressured to 400 psig and stirred at 30°C for 30 minutes. The autoclave was vented and opened, and the polymer

product isolated. The yield of linear polyethylene was 42.4 g. This material had a calculated weight-average molecular weight of 2,487,000, a peak-maximum molecular weight of 3,204,000 and a calculated molecular weight distribution of 1.49.

In accordance with the invention, polymerizations carried out at lower temperatures will lead to polymers with higher molecular weights and polymerizations carried out at higher pressures will obtain polymers of higher molecular weight.

These very high molecular weight polyethylenes having narrow molecular weight distributions have been found to be highly desireable fn high tensile strength applications, such as in the production of oriented polyethylene fibers by gel-spinning.

The principle of the invention and the best mode contemplated for applying that principle have been described. It is to be understood that the foregoing is illustrative only and that other means and techniques can be employed without departing from the true scope of the invention defined in the following claims.

CLAIMS

1. Polyethylenes having a weight-average molecular weight greater than about 1×10^6 and a molecular weight distribution less than about 3.0.

2. The polymer of claim 1 wherein the molecular weight distribution ranges from about 1.3 to about 2.0.

3. The polymer of claim 2 having a weight-average molecular weight ranging from about 2×10^6 to about 25×10^6.

4. The polymer of claim 3 wherein the weight-average molecular weight ranges from about 2×10^6 to about 6×10^6.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/04366

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 F 110/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	Chemical Abstracts, volume 110, no. 6, 6 February 1989, (Columbus, Ohio, US), Sajkiewicz, P.: "Ultrahigh-molecular-weight oriented polyethylene- preparation and preliminary structural studies of films ", see page 20, abstract 399652d, & Polimery (Warsaw) 1988, 33(6), 220- 224 --	1,3,4
X	Chemical Abstracts, volume 106, no. 4, 26 January 1987, (Columbus, Ohio, US), Kusy, R. P.: "Molecular weight distribution of a bulk ultra-high molecular weight polyethylene product-Impax 5M+ UHMW-NAT. ", see page 297, abstract 23217x, & J. Biomed. Mater. Res. 1986, 20(9), 1373-1389 --	1,3,4

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
5th November 1990	2[illegible] 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	[illegible] TORIBIO

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	Chemical Abstracts, volume 107, no. 2, 13 July 1987, (Columbus, Ohio, US), see page 13, abstract 7809g, & JP, A, 61283606 (Easily-dissolvable ultrahigh-molecular weight polyethylene powders)	1
X	Chemical Abstracts, volume 97, no. 22, 29 November 1982, (Columbus, Ohio, US), Baulin, A.A. et al.: "Preparation of high-molecular-weight polyethylene on supported Ziegler-Natta catalysts ", see page 3, abstract 182911f, & Plast. Massy 1982, (8), 6- 8	1
A	Chemical Abstracts, volume 101, no. 16, 15 October 1984, (Columbus, Ohio, US), Wagner, H.L. et al.: "Aspects of the characterization of ultra-high molecular weight polyethylene ", see page 23, abstract 131428x, & Polym. Master. Sci. Eng. 1984, (50), 53- 57	1-4
A	DE, C2, 2724096 (SEVEROVA, N.N. ET AL.) 30 November 1978, see column 2, line 3	1-4

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/04366

SA 39229

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 27/09/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-C2- 2724096	30/11/78	NONE	

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

EPO FORM P0479

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7/7/1
DIALOG(R)File 351:Derwent WPI

004541655
WPI Acc No: 1986-044999/198607
Poly(1-butene) resin with improved rigidity and impact resistance - comprises 1-butene and 2-12C olefin e.g. ethylene, propylene, pentene, octene etc
Patent Assignee: MITSUI PETROCHEM IND CO LTD (MITC)
Number of Countries: 001 Number of Patents: 002
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
JP 60262804	A	19851226	JP 84118089	A	19840611	198607	B
JP 93059922	B	19930901	JP 84118089	A	19840611	199338	

Priority Applications (No Type Date): JP 84118089 A 19840611
Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
JP 60262804	A		11		
JP 93059922	B		9	C08F-010/08	Based on patent JP 60262804

Abstract (Basic): JP 60262804 A
Poly(1-butene) resin comprises 100-99 mol.% of 1-butene and 0-1 mol % of 2-12C olefin where the resin has (a) intrinsic viscosity of 1.5-4.0 dl/g, (b) Mw/Mn of less than 6 and isotactic value of more than 95%.
Specifically, the olefin includes e.g. ethylene, propylene, 1-pentene, 1-octene, 1-decene or 1-dodecene. The monomer is polymerised at 20-200 deg.C, 2-50 kg/cm2 in presence of catalyst.
The catalyst comprises (1) solid Ti cpd., (2) trialkyl aluminum cpd., and (3) organic Si cpd. e.g. triethanol methoxysilane, triethyl ethoxysilane, tripropyl methoxysilane, vinyl triethoxysilane, phenyl triethoxysilane or tetraethoxysilane.
USE/ADVANTAGE - The resin has higher rigidity and crystalline transition speed, and superior resistance to creep and impact. The resin is used as pipe material. (11pp Dwg.No.0/0)
Derwent Class: A17
International Patent Class (Main): C08F-010/08
International Patent Class (Additional): C08F-004/654
?

T 8/7

8/7/1
DIALOG(R)File 351:Derwent WPI

007192245
WPI Acc No: 1987-189254/198727
Random copolymer of 1-polybutylene and alpha polyolefin - has narrower mol. wt. distribution, improved transparency and mechanical strength
Patent Assignee: MITSUI PETROCHEM IND CO LTD (MITC)
Number of Countries: 001 Number of Patents: 002
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
JP 62119213	A	19870530	JP 85258498	A	19851120	198727	B
JP 94104699	B2	19941221	JP 85258498	A	19851120	199504	

Priority Applications (No Type Date): JP 85258498 A 19851120
Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
JP 62119213	A		18		
JP 94104699	B2		13	C08F-210/08	Based on patent JP 62119213

Abstract (Basic): JP 62119213 A
Random copolymer comprises (a) 1-butene and (b) other 3-20C alpha-olefin having (1) 1-butene content of 60-98 mol.%, (2) alpha-olefin content of 2-40 mol.%, (3) intrinsic viscosity measured in decalin at 135 deg.C of 0.5-6 dl/g, (4) Mw/Mn measured with GPC of less than 3, (5) melting point measured with a differential scanning calorimeter of 40-130 deg.C, (6) crystalline degree measured with an X-ray diffractometry, of 5-60%, (7) soluble contents in boiled methyl acetate of less than 1 wt.%, (8) soluble contents in a mixed solvent of acetone and n-decane (1/1 by vol.) at 10, of less than 4 x (eta)-1.2 (eta is intrinsic viscosity of the polymer) and (9) standard deviation of ingredients distribution in the copolymer of less than 10 mol.%. The signal derived from 2 methylene gps. among 2 neighbouring tert. carbons in the copolymer chain, is not detected in a 13C-NMR spectrum.
USE/ADVANTAGE - The copolymer has improved transparency and narrower molecular wt. distribution. The copolymer is used for moulding materials. The article (e.g. films or sheets) obtd. has reduced adhesion properties and tensile strength. :
Derwent Class: A17
International Patent Class (Main): C08F-210/08
International Patent Class (Additional): C08F-004/64; C08L-023/18; C08L-101/00; C08F-210/08; C08F-210-00
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